

PATENT ABSTRACTS OF JAPAN

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(54) METHOD FOR PRODUCING POROUS FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing a porous film having high porosity and air permeability and high mechanical strength and shrinkage and high heat resistance as well, to provide the porous film obtained by the above method, to provide a battery separator comprising the above film, and to provide batteries and capacitors using the above separators.

SOLUTION: This method for producing the porous film comprises the steps of melting and kneading a resin composition comprising a resin component comprising a polyolefin and a rubber having crosslinkable unsaturated bonds and a solvent, forming the resultant melt kneaded product into a sheet form, and then subjecting the sheet form to orientation treatment and desolvation treatment, wherein this method comprises an ultraviolet irradiation step in addition to the above-mentioned steps. The 2nd objective porous film obtainable by the above method is provided. The 3rd objective battery separator comprises the above porous film. The 4th objective batteries and the other objective capacitors using the above separators are also provided, respectively.

* NOTICES *

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- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the cell and capacitor which use the separator for cells which consists of a porosity film which may be obtained by the manufacturing method of a porosity film, and this manufacturing method, and this porosity film, and this separator for cells.

[0002]

[Description of the Prior Art]The porosity film is used for the separator for cells, electrolytic condenser barrier membrane, a moisture permeation water blocking material, various filters, etc. Especially, a light weight, higher electromotive force, and high energy are obtained as a cell, and, moreover, the separator for cells attracts attention as an important member of a lithium secondary battery with little self-discharge.

It is expected also as members forming of the battery for electromobiles from now on.

[0003]Until now, some proposals about the improvement in heat-resistant of the separator for lithium secondary batteries are made focusing on the polyolefine content porosity film. For example, in JP,10-12211,A, a polyolefine content porosity film is made to laminate the nonwoven fabric of glass fiber, etc., and they are used. There are many using the high molecular compound made to construct a bridge by the technique of making it polymerize after film production etc. like JP,3-245457,A or JP,3-193125,A. Not only like a presentation side but like JP,5-74444,A, the proposal in the structural face in a cell of pasting up the flash part from the polar plate of a separator is also made. Although the porosity film containing rubber other than polyolefin resin is indicated by JP,1-18091,B, JP,9-169867,A, and JP,6-153023,A, these are not the things aiming at the improvement in heat-resistant.

[0004]The resin which forms the film fuses the separator for rechargeable lithium-ion batteries,

ionic permeability is lost by making a membranous hole blockade in the case of unusual heating of a cell, and it has a shutdown (SD) function which prevents the further heating by current. However, since the rise in heat is very rapid when the abnormalities through which a short-circuit current flows into a cell by the external short circuit of a cell, etc. occur, even if SD function is fully revealed, the danger that temperature has already reached a temperature higher than SD temperature of a separator for whether your being Haruka is high. In such a case, a separator will be in a molten state thoroughly, and when there is existence of a foreign matter and the lithium dendrite which deposited especially, there are a fracture and a danger of the amniorrhexis being carried out, and an anode and a negative electrode carrying out direct contact, and being in a short condition, easily. In particular, the internal pressure in a cell increases in an overcharging condition etc., and the danger that high voltage will add and carry out an amniorrhexis short circuit increases in a thickness direction further.

[0005]

[Problem(s) to be Solved by the Invention]Also in the case where it is exposed to the elevated temperature and a high pressure state which the purpose of this invention has high porosity and the Takamichi temperament, and a mechanical strength and contraction are good and describe above. A manufacturing method of a porosity film which has the high heat resistance of the grade which can maintain the shape and which is especially used suitably as a separator for rechargeable lithium-ion batteries, it is providing the cell and capacitor which use the separator for cells which consists of a porosity film obtained by this manufacturing method, and this porosity film, and this separator for cells.

[0006]

[Means for Solving the Problem]This invention persons by irradiating with ultraviolet rays as one process at the time of manufacturing a porosity film, as a result of inquiring wholeheartedly in order to solve said SUBJECT, While promoting crosslinking reaction of raw resin which constitutes a porosity film, it finds out that improvement in a void content or breathability can be aimed at, and came to complete this invention.

[0007]Namely, a gist of this invention carries out melt kneading of the resin composition containing a resinous principle and a solvent containing the rubbers which have an unsaturated bond of (1) polyolefine and cross-linking, In a manufacturing method of a porosity film which has the process of fabricating an obtained melt kneading thing to a sheet shaped, and performing stretching treatment and desolvation treatment of this sheet-shaped molded product. A porosity film which may be obtained by manufacturing method of a porosity film which has the process of irradiating with ultraviolet rays, and a manufacturing method of a porosity film given in (2) aforementioned (1), (3) It is related, without a capacitor which uses a cell which uses a separator for cells and a separator for cells given in (4) aforementioned (3) which consist of a porosity film of the aforementioned (2) statement, and a separator for cells

given in (5) aforementioned (3).

[0008]

[Embodiment of the Invention]The publicly known wet forming-membranes method can be used for the manufacturing method of the porosity film of this invention, for example, After carrying out stretching treatment of the sheet-shaped molded product obtained by cooling after extruding the resin composition containing a resinous principle and a solvent to heat melting and extruding the melt kneading thing obtained by kneading to a sheet shaped and carrying out desolvation treatment subsequently, it is preferred to perform the exposure of ultraviolet rays.

[0009]In this invention, polyolefine is used as one of said the resinous principles. As this polyolefine, ethylene, propylene, 1-butene, The homopolymer of olefins, such as 4-methyl-1-pentene and 1-hexene, From a viewpoint of high-intensity-izing of the porosity film which copolymers, these mixtures, etc. are mentioned and is obtained especially. More preferably, the ultrahigh-molecular-weight polyolefine more than 1.5×10^6 is still more preferably preferred, and especially ultra high molecular weight polyethylene is [more than weight-average-molecular-weight 5×10^5 / more than 1×10^6] preferably preferred. Weight average molecular weight can be measured by the method of a statement in the below-mentioned example.

[0010]There is many tangle of ultrahigh-molecular-weight polyolefine in the case of melt kneading, from a viewpoint from which sufficient film strength is obtained, as for the content of said ultrahigh-molecular-weight polyolefine in said polyolefine, 1 % of the weight or more is preferred, its 50 to 100 % of the weight is more preferred, and its 60 to 90 % of the weight is still more preferred.

[0011]As for the loadings of said polyolefine, 50 to 95 % of the weight is preferred among the resinous principle of said resin composition, and its 60 to 90 % of the weight is more preferred. As for these loadings, 95 or less % of the weight is preferred from a viewpoint which 50 % of the weight or more is preferred, uniform kneading is easy, and thickness nonuniformity and characteristic nonuniformity do not produce from a viewpoint of raising film strength.

[0012]The rubbers which have an unsaturated bond of cross-linking as one of everything [the] but said resinous principle in this invention are used. Especially as these rubbers, with the intensity revealed with ultrahigh-molecular-weight polyolefine. Furthermore also in the high temperature region which exceeded, the melting point (about 141°C) of ultrahigh-molecular-weight polyolefine Shape maintenance nature, The thing which can form the structure of cross linkage between ultrahigh-molecular-weight polyolefines in a crosslinking treatment process from a viewpoint which may demonstrate a mechanical strength and which has a C=C double bond especially in a main chain is preferred. Especially, an unsaturation condensation alicyclic compound or the ring-opening-polymerization object of the derivative has the aliphatic series ring and double bond originating in the monomeric unit in the main chain, and since it can

expect the heat-resistant improvement in efficient formation of the structure of cross linkage, and the porosity film obtained, it is preferred. As for this ring-opening-polymerization object, hydrogenation of a part of the double bond may be carried out.

[0013]The monomer which has the structure which replaced end hydrogen of the low grade hydrocarbon which has a double bond in an end by ethylene as an example of these rubbers is polymerized, and the resin which has the structure which the methylene group has combined with the main chain, for example, polybutadiene etc., is mentioned. The thing of three series explained below is mentioned as said unsaturation condensation alicyclic compound.

[0014]As the first series, the unsaturated compound which has a double bond included in a main chain in one of the rings is mentioned after ring opening polymerization among what is classified as a condensation alicyclic compound in a narrow sense. Some of hydrogen atoms of those unsaturated compounds can use it as an unsaturation condensation alicyclic compound also including the derivative which replaced other substituents. As this example, it is [bicyclo]. [3.2.0]Bicyclo [hept 6-ene,] [4.2.0]Oct 7-ene, those derivatives, etc. are mentioned.

[0015]As the second series, the unsaturated compound which has a double bond included in a main chain in one of the rings is mentioned after ring opening polymerization among what is classified as a bridged cyclic compound. Some of hydrogen atoms of those unsaturated compounds can use it as an unsaturation condensation alicyclic compound also including the derivative which replaced other substituents. As this example, it is [bicyclo]. [2.2.1]Bicyclo [hept 5-ene (in this specification, it may be called norbornene),] [2.2.1]Bicyclo [norbornene derivatives, such as hept 5-ene- 2,3-dicarboxymethyl ester,] [2.2.2]Oct 2-ene, those derivatives, etc. are mentioned.

[0016]As the third series, it is owner ****, and has condensation alicycle, and the compound which has an aliphatic series ring and a double bond in a main chain is mentioned after ring opening polymerization. As this example, it is tricyclo. [5.2.1.0^{2,6}] Deca- 3,8-diene (dicyclopentadiene), tetracyclo dodecen, those derivatives, etc. are mentioned.

[0017]In these unsaturation condensation alicyclic compounds, a viewpoint to norbornene and norbornene derivatives, such as feeding, are preferred. These unsaturation condensation alicyclic compounds are independent, or can mix two or more sorts, or can carry out ring opening polymerization one by one.

[0018]As a ring-opening-polymerization object of said unsaturation condensation alicyclic compound, poly norbornene etc. are used preferably, and poly norbornene with high weight average molecular weight is especially used preferably from a viewpoint of dispersibility.

[0019]Such rubbers by using preferably with said ultrahigh-molecular-weight polyolefine, especially ultra high molecular weight polyethylene, Also in a high temperature region, the shape and the mechanical strength of a porosity film are maintainable, Heat resistance can be

improved by the crosslinking treatment by the UV irradiation which is furthermore one feature of the manufacturing method of this invention. For example, since the state where the anode and the negative electrode were separated can be maintained also when this separator is exposed to an elevated temperature and high voltage in the cell which uses this porosity film as a separator for cells, the safety of this cell will improve.

[0020]As for the loadings of said rubbers, 1 to 50 % of the weight is preferred among the resinous principle of said resin composition, and its 1 to 20 % of the weight is more preferred. As for these loadings, the viewpoint of the maintenance and improvement in the intensity of a porosity film and breathability which 1 % of the weight or more is preferred, and is obtained from a viewpoint of improvement in the crosslinking density which contributes to heat resistance to 50 or less % of the weight is preferred.

[0021]Resin of said rubbers and others which can construct a bridge may be arbitrarily used as a resinous principle. As such resin, denaturation polyolefines, such as an ethylene-acrylic monomer copolymer and an ethylene-vinylacetate copolymer. Thermoplastic elastomer, for example, high, inside, and low density polyethylene, such as a polystyrene system, a polyolefin system, a polydien system, a VCM/PVC system, and a polyester system, polypropylene, those copolymers, etc. are mentioned.

[0022]These resin is independent, or two or more sorts can be mixed and it can be used. As for the loadings, 5 to 50 % of the weight is preferred among the resinous principle of said resin composition, and its 10 to 40 % of the weight is more preferred.

[0023]The rubbers which have an unsaturated bond of said polyolefine and cross-linking as said solvent. What was furthermore excellent in the solubility of thermoplastic elastomer preferably. For example, the non volatile solvent which the mineral oil fraction corresponding to these in aliphatic series, such as nonane, Deccan, an undecane, a dodecane, a decalin, and a liquid paraffin, or cyclic hydrocarbon, and the boiling point, etc. are mentioned, and contains many alicyclic hydrocarbon, such as a liquid paraffin, is preferred. As loadings of a solvent, kneading torque, rolling, and extension stress are proper, and it excels in productivity. In said resin composition from a viewpoint that the porosity film in which the neck in in the dice exit at the time of sheet-izing did not become a problem, either, but it could fabricate good, and the fine porosity of the moderate and homogeneous aperture was moreover formed is obtained, desirable -- five to resinous principle 30 weight section, and 70 to solvent 95 weight section -- more -- desirable -- ten to resinous principle 30 weight section, and a solvent -- it is considered as ten to resinous principle 25 weight section, and 75 to solvent 90 weight section still more preferably 70 to 90 weight section.

[0024]To said resin composition, additive agents, such as an antioxidant, an ultraviolet ray absorbent, a color, a nucleating agent, paints, and a spray for preventing static electricity, can be added in the range which does not spoil the purpose of this invention by request.

[0025]It mixes to uniform slurry form and the resin composition which consists of a resinous principle and a solvent is prepared, for example. Then, although melting kneading is carried out and this resin composition is fabricated to a sheet shaped, This process should just follow a publicly known method, and using a Banbury mixer, a kneader, etc., under suitable temperature conditions, preferably, knead it and it ranks second by a batch type at 100-200 **, It may put between the cooled metal plate or roll, it may quench, and may be made a sheet-shaped molded product by quenching crystallization, and a sheet-shaped molded product may be obtained using the extrusion machine etc. which attached the T die etc. Thus, although the thickness in particular of the sheet-shaped molded product obtained is not limited, its 3-20 mm is preferred.

[0026]Especially as a method of the stretching treatment of said sheet-shaped molded product, it is not limited, and it may be the combination of the usual tenter method, the rolling method, tubular film processes, or these methods, and any methods, such as uniaxial stretching and biaxial stretching, can be applied. In the case of biaxial stretching, any of in-every-direction simultaneous extension or one by one extension may be sufficient, but in-every-direction simultaneous extension is preferred. 100-150 ** of temperature of stretching treatment is 115-130 ** more preferably.

[0027]The thickness of the sheet before extension is 0.2-0.8 mm more preferably 0.2-1.2 mm, and 50-150 micrometers of thickness after extension are 60-100 micrometers more preferably. The speed of extension is 3 mm/second or less more preferably 5 mm/second or less, and if it is this within the limits, since it does not raise an extension piece in the middle of extension, it is preferably preferred.

[0028]Desolvation treatment is a process which removes a solvent from a sheet-shaped molded product and in which fine porous structure is made to form, for example, can be performed by removing the solvent which washes a sheet-shaped molded product with a solvent, and remains. As a solvent, hydrocarbon, such as pentane, hexane, heptane, and Deccan, Easy-volatility solvents, such as ether, such as hydrocarbon fluoridation, such as chlorinated hydrocarbons, such as a methylene chloride and a carbon tetrachloride, and ethanetrifluoride, diethylether, and dioxane, are mentioned, and these are independent, or can mix and use two or more sorts. The method of the cleaning method in particular using this solvent not being limited, for example, a sheet-shaped molded product being immersed into a solvent, and extracting a solvent, the method of carrying out the shower of the solvent to a sheet-shaped molded product, etc. are mentioned. Desolvation treatment may be performed before extension. For example, after carrying out desolvation treatment of the sheet-shaped constituent, stretching treatment may be presented, or desolvation treatment may be performed before stretching treatment, and desolvation treatment may be again performed after stretching treatment.

[0029]In this invention, a rolling process may be further performed before and after extension and desolvation treatment. For example, after carrying out the rolling process of the sheet-shaped molded product as it is, stretching treatment and desolvation treatment (the point may be [order of extension and deliquoring] sufficient as any) may be performed. Or it may be a mode which may perform a rolling process between stretching treatment and desolvation treatment, for example, performs desolvation treatment before a rolling process, performs stretching treatment and desolvation treatment (the point of an order of extension and deliquoring may be sufficient as any) again after a rolling process, and removes a residual solvent.

[0030]Heat pressing etc. perform this rolling process, and it is preferably fabricated in the thickness of 1/5 to 1/20 to the thickness of the sheet-shaped molded product before a rolling process not less than 100 **, heating at 100-140 ** more preferably.

[0031]After forming said resinous principle by these publicly known methods, it is preferred to carry out UV irradiation to the obtained film. The ultraviolet rays which UV irradiation is preferred and do not have distribution of wavelength substantially in 200 nm or less. It carries out by irradiating with the ultraviolet rays which do not have distribution of wavelength substantially in 250 nm or less more preferably from a viewpoint of maintaining sufficient film strength, to a for [0.5 to 20 minutes] grade, and the film obtained after membrane formation. All or a part of double bonds of the resin origin which has cross-linking by this UV irradiation disappear. In the porosity film obtained, between resin, or the resin concerned concerned and polyolefine, bridge construction will arise, and the heat resistance (amniorrhesis-proof nature under an elevated temperature and high voltage) of a porosity film will maintain and improve. Simultaneously with heat-resistant improvement, in this invention, a void content and breathability are raised by performing UV irradiation. When improvement in the void content and the breathability of a porosity film was performed by adjusting raw resin etc. suitably and it asked for high void content and breathability conventionally, the raw resin which can be used was restricted and, as a result, there was a case where a sacrifice fake colander was not obtained. about the intensity of a porosity film. However, in this invention, since the film which has sufficient intensity first is obtained, it subsequently irradiates with ultraviolet rays and a void content and breathability are raised, the outstanding porosity film a void content and whose breathability whose intensity was enough and moreover improved more is obtained.

[0032]Said crosslinking treatment impregnates with the methanol solution which contains remaining as it is or a polymerization initiator in the film after membrane formation, for example, after drying methanol which is a solvent, a low pressure mercury lamp or a high-pressure mercury-vapor lamp is used for it, irradiates with ultraviolet rays, and is performed. It is preferred to use for the exposure of ultraviolet rays said mercury-vapor lamp which generates the ultraviolet rays which do not have distribution of wavelength substantially in 250

nm or less from a viewpoint of maintaining sufficient film strength.

[0033]The heat setting (heat setting) of the obtained porosity film may be carried out from a viewpoint which prevents heat contraction following said crosslinking treatment process. What is necessary is for the temperature at the time of carrying out a heat setting to be 110-140 **, and just to perform it for about 0.5 to 2 hours, for example.

[0034]As thickness of the porosity film produced by making it above, 10-50 micrometers is 15-40 micrometers more preferably. If it is this within the limits, the performance of a cell of using the separator for cells which consists of this porosity film is good, and preferred. As the permeability, it is 750 or less seconds/100 cc more preferably 800 or less seconds/100 cc. It is 150 seconds/100 cc or more more preferably 100 seconds/100 cc or more. If it is within the limits which requires permeability, the perviousness and solution retention of an electrolysis solution are good, moreover electrical resistance is proper, and a good cell can be assembled by using this porosity film as a separator. 30 to 70% of a void content is desirable, and is more desirable. [35 to 50% of] If a void content is said within the limits, fine porosity distribution will be proper and, moreover, the short circuit of a cell will be suppressed also in an overcharging condition. It thrusts, and more than 3N/25micrometer of intensity is preferred, and more than its 4N/25micrometer is more preferred. It has sufficient intensity, without thrusting, and carrying out the amniorrhaxis, if intensity is said within the limits. The viewpoint that sufficient mechanical strength is obtained to a gel fraction is 50 to 90% preferably. The various characteristics of these porosity films can be measured by the method of indicating in the below-mentioned example.

[0035]The porosity film of this invention with high membrane characteristics also under an elevated temperature and a high pressure state, It has the high heat resistance of the grade which can maintain the shape, and can be especially used conveniently as a separator for rechargeable lithium-ion batteries, and the application as the separator of a capacitor, an oil absorbing sheet, and a filter is also still more possible.

[0036]As a cell of this invention, coming [said porosity film] to use as a separator, it may be the same as that of a cell [be / just publicly known / about the structure, structure material, and a manufacturing method / what is necessary], and there is no limitation in particular. Since the porosity film of this invention is used for this cell as a separator, it is excellent in safety. A capacitor can also be obtained by using said porosity film as a separator. This capacitor can be manufactured like a publicly known capacitor, and is excellent in safety.

[0037]

[Example]Although this invention is explained still in detail based on an example, this invention is not limited only to this example. About the various characteristics of the porosity film obtained in each example and a comparative example, it measured in the following way.

[0038](1) o-dichlorobenzene was measured at 135 ** to the solvent again using the gel

permeation chromatograph by weight-average-molecular-weight Waters "GPC-150C", using "Shodex-80M" by Showa Denko K.K. as a column. Data processing was performed using the data processing system by TRC. The molecular weight was computed on the basis of polystyrene.

[0039](2) Film thickness (micrometer) was measured by film thickness 1 / 10000 thickness gage.

[0040](3) The porosity film of the void content measuring object was clipped to a round form 6 cm in diameter, the volume and weight were found, and it calculated using the following formula from them.

Void content (volume %) = $100 \times [\text{Mean density of the resinous principle of the volume (cm}^3\text{)} - \text{weight (g) / porosity (g/cm}^3\text{)}] / \text{volume (cm}^3\text{)}$ [0041](4) Permeability (Gurley value)

Permeability (a second / 100cc) was measured based on JIS P8117.

[0042](5) It examined by thrusting and thrusting using the compression testing machine made from Examination KATO Tech "KES-G5." Maximum load was read and pierced from the obtained load change curve, and it was considered as intensity (N). The needle was performed at 2 cm/second in speed using the with 0.75 mm in diameter, and a curvature radius [of a tip] of 0.5 mm thing. All values were converted into 25 micrometers in thickness.

[0043](6) The film cut off to the round form with a contraction diameter of 6 cm was read by 144dpi with the image scanner, area was changed into the number of pixels, and it was considered as the blank value. Next, the film was held in the 1-hour constant temperature dryer at 105 **, it read by 144dpi with the after-extraction image scanner, area was changed into the number of pixels, and it was considered as the value after heat treatment. From the blank and the number of area pixels after heat treatment, it asked for R_1 (contraction) (%) with the following formula.

$R_1 = 100 \times (P_0 - P_1) / P_0$ (the number of pixels before P_0 : heat contraction, P_1 : the number of pixels after heat contraction)

[0044](7) The gel fraction porosity film was cut in angle of 4 cm x 4 cm, and it put by the metallic mesh (5 cm x 5 cm), and was considered as the sample of 5 cm x a 5-cm angle. The initial mass of this sample was measured, it is immersed into 100 ml of m-xylene (139 ** of boiling points), temperature up is carried out, xylene was boiled for 3 hours, after-extraction washing desiccation was carried out, and gel fraction R_2 (%) was measured from the weight change.

R_2 (%) = $100 \times P1 / P0$ [Weight after $P0$: initial-mass (g) $P1$: boil xylene treatment (g)]

[0045](8) Between zippers was attached as 10 mm, the porosity film of the shape of a strip of paper with a heat-resistant width of 3 mm was set to product thermal-stress-distortion analysis

apparatus TMA/SS made from SEIKO electron 100, and temperature up was carried out by the heating rate of 2 °C / min. Temperature at the time of a strip-of-paper-like porosity film fracturing was made into the heat-resistant fracture temperature (°C) as a heat-resistant index.

[0046] example 1 liquid-paraffin 85 weight section and ultra high molecular weight polyethylene (the Mitsui Chemicals, Inc. make.) Trade name : Hizex Million 240S, the melting point of 136 °C, 2x10⁶ 70 % of the weight of weight average molecular weight, poly polynorbornene rubber (norbornene ring-opening-polymerization object powder and the Nippon Zeon Co., Ltd. make.) Trade name : No Sorex NB and more than weight-average-molecular-weight 2x10⁶ 8 % of the weight, polyolefin system thermoplastic-elastomer TPE821 (the Sumitomo Chemical Co., Ltd. make.) Trade name : mixture 15 weight section which consists of TPE821 and 22 % of the weight of polyethylene polypropylene copolymers. It kneaded at 160 °C with the twin screw extruder (Toshiba Machine, TEM-35B), and for the fish tail dice, it let it pass to the sizing die, and quenched to dry ice temperature (-30 °C) after extrusion, and the gel molded product about 8 mm thick was produced. After pressing this by a spacer thickness of 9 mm after preheating for 5 minutes at 115 °C and holding it for 3 minutes with a hot press machine, quenching was carried out at the pressing machine cooled for water temperature, and the gel sheet about 110 mm thick was obtained. This sheet was extended about 3.2x3.2 times after preheating in 127 °C with the batch type simultaneous biaxial-stretching machine (made in [the Iwamoto factory] and BIX-712-S), and the gel film about 90 micrometers thick was obtained. The stretching speed was set [second] up in 4 mm / . It fixed to the square frame made from SUS, and the obtained gel film extracted the solvent by n-heptane of three baths, dried heptane at the room temperature, and obtained the porosity film. subsequently, the conveyor type high-pressure mercury-vapor lamp irradiation equipment (eye graphics company make.) which enabled generating of the ultraviolet rays which do not have distribution of wavelength substantially in 200 nm or less fixed to the frame made from SUS UV irradiation for 15 minutes is performed in UE021-203C, the output of 2 kW, and conveyor speed 3 m/min, Supply in a dryer as it is after that, and at 117 °C at 85 °C for 12 hours 2 hours, Heat setting processing was performed one by one, eventually, it thrust and 24 micrometers in thickness, 40% of a void content, and 470 seconds/100 cc of permeability obtained the with intensity 6N/25micrometer, 13% of contraction, the gel fraction of 72%, and a heat-resistant fracture temperature of not less than 200 °C porosity film.

[0047] In comparative example 1 Example 1, except not having performed UV irradiation, it presupposed that it is the same, and it thrust and 24 micrometers in thickness, 35% of a void content, and 670 seconds/100 cc of permeability obtained the with intensity 6.5N/25micrometer, 12% of contraction, the gel fraction of 75%, and a heat-resistant fracture temperature of not less than 200 °C porosity film.

[0048] In example 2 Example 1, 88 % of the weight of ultra high molecular weight polyethylene

and the mixture which consists of 12 % of the weight of poly polynorbornene rubber are used, 2 mm/[a second and] and UV irradiation time for 125 ** and a stretching speed For 10 minutes, [the temperature at the time of extension] Heat setting processing was made the same except 85 ** having performed one by one at 130 ** for 2 hours for 12 hours, 23 micrometers in thickness, 33% of a void content, and 650 seconds/100 cc of permeability thrust, and the with intensity 7N/25micrometer, 3% of contraction, the gel fraction of 80%, and a heat-resistant fracture temperature of not less than 240 ** porosity film was obtained.

[0049]In comparative example 2 Example 2, except not having performed UV irradiation, it presupposed that it is the same, and it thrust and 23 micrometers in thickness, 30% of a void content, and 880 seconds/100 cc of permeability obtained the with intensity 7.5N/25micrometer, 3% of contraction, the gel fraction of 78%, and a heat-resistant fracture temperature of not less than 240 ** porosity film.

[0050]example 3 liquid-paraffin 85 weight section and ultra high molecular weight polyethylene (the Mitsui Chemicals, Inc. make.) Trade name : Hizex Million 240S, the melting point of 136 **, 2×10^5 70 % of the weight of weight average molecular weight, poly polynorbornene rubber (norbornene ring-opening-polymerization object powder and the Nippon Zeon Co., Ltd. make.) Trade name : No Sorex NB and more than weight-average-molecular-weight 2×10^5 8 % of the weight, polyolefin system thermoplastic-elastomer TPE821 (the Sumitomo Chemical Co., Ltd. make.) Trade name : mixture 15 weight section which consists of TPE821 and 22 % of the weight of polyethylene polypropylene copolymers, It kneaded at 160 ** with the twin screw extruder (Toshiba Machine, TEM-35B), and for the fish tail dice, it let it pass to the sizing die, and quenched to dry ice temperature after extrusion, and the gel molded product about 8 mm thick was produced. After pressing this by a spacer thickness of 9 mm after preheating for 5 minutes at 115 ** and holding it for 3 minutes with a hot press machine, *** quenching was carried out at the pressing machine cooled for water temperature, and the gel sheet about 110 mm thick was obtained. This sheet was extended about 3.2x3.2 times after preheating in 127 ** with the batch type simultaneous biaxial-stretching machine (made in [the Iwamoto factory] and BIX-712-S), and the gel film about 90 micrometers thick was obtained. The stretching speed was set [second] up in 4 mm / . It fixed to the square frame made from SUS, and the obtained gel film extracted the solvent by n-heptane of three baths, dried heptane at the room temperature, and obtained the porosity film. subsequently, the conveyor type high-pressure mercury-vapor lamp irradiation equipment (eye graphics company make.) which enabled generating of the ultraviolet rays which do not have distribution of wavelength substantially in 250 nm or less fixed to the frame made from SUS UV irradiation for 15 minutes is performed in UE021-203C, the output of 2 kW, and conveyor speed 3 m/min, Supply in a dryer as it is after that, and at 117 ** at 85 ** for 12 hours 2 hours, Heat setting processing was performed one by one, eventually, it thrust and 24 micrometers in thickness, 39% of a void content, and 480

seconds/100 cc of permeability obtained the with intensity 6.5N/25micrometer, 12% of contraction, the gel fraction of 74%, and a heat-resistant fracture temperature of not less than 200 °C porosity film.

[0051]It is supposed that it is the same except the conveyor type high-pressure mercury-vapor lamp irradiation equipment which enabled generating of the ultraviolet rays which do not have distribution of wavelength substantially in 200 nm or less in example 4 Example 3 having performed UV irradiation for 15 minutes. It thrust and 24 micrometers in thickness, 40% of a void content, and 470 seconds/100 cc of permeability obtained the with intensity 6N/25micrometer, 13% of contraction, the gel fraction of 72%, and a heat-resistant fracture temperature of not less than 200 °C porosity film.

[0052]In comparative example 3 Example 3, except not having performed UV irradiation, it presupposed that it is the same, and it thrust and 24 micrometers in thickness, 35% of a void content, and 670 seconds/100 cc of permeability obtained the with intensity 6.5N/25micrometer, 12% of contraction, the gel fraction of 75%, and a heat-resistant fracture temperature of not less than 200 °C porosity film.

[0053]In example 5 Example 3, 88 % of the weight of ultra high molecular weight polyethylene and the mixture which consists of 12 % of the weight of poly polynorbornene rubber are used. The UV irradiation time by the conveyor type high-pressure mercury-vapor lamp irradiation equipment which enabled generating of the ultraviolet rays which do not have [the temperature at the time of extension] distribution of wavelength for 125 °C and a stretching speed substantially in 2 mm /and 250 nm or less a second For 10 minutes, Heat setting processing was made the same except 85 °C having performed one by one at 130 °C for 2 hours for 12 hours, 23 micrometers in thickness, 33% of a void content, and 680 seconds/100 cc of permeability thrust, and the with intensity 7.5N/25micrometer, 3% of contraction, the gel fraction of 81%, and a heat-resistant fracture temperature of not less than 240 °C porosity film was obtained.

[0054]It is supposed that it is the same except the conveyor type high-pressure mercury-vapor lamp irradiation equipment which enabled generating of the ultraviolet rays which do not have distribution of wavelength substantially in 200 nm or less in example 6 Example 3 having performed UV irradiation for 10 minutes. It thrust and 23 micrometers in thickness, 33% of a void content, and 650 seconds/100 cc of permeability obtained the with intensity 7N/25micrometer, 3% of contraction, the gel fraction of 80%, and a heat-resistant fracture temperature of not less than 240 °C porosity film.

[0055]In comparative example 4 Example 5, except not having performed UV irradiation, it presupposed that it is the same, and it thrust and 23 micrometers in thickness, 30% of a void content, and 880 seconds/100 cc of permeability obtained the with intensity 7.5N/25micrometer, 3% of contraction, the gel fraction of 78%, and a heat-resistant fracture

temperature of not less than 240 °C porosity film.

[0056]

[Table 1]

	紫外線 (nm)	フィル膜厚 (μm)	空隙率 (%)	J-V通気度 (秒/100cc)	突き刺し強度 (N/25μm)	収縮率 (%)	ゲル分率 (%)	耐熱破断温度 (°C)
実施例 1	>200	2.4	4.0	4.70	6	1.3	7.2	≥200
比較例 1	—	2.4	3.5	6.70	6.5	1.2	7.5	≥200
実施例 2	>200	2.3	3.3	6.50	7	3	8.0	≥240
比較例 2	—	2.3	3.0	8.80	7.5	3	7.8	≥240
実施例 3	>250	2.4	3.9	4.80	6.5	1.2	7.4	≥200
実施例 4	>200	2.4	4.0	4.70	6	1.3	7.2	≥200
比較例 3	—	2.4	3.5	6.70	6.5	1.2	7.5	≥200
実施例 5	>250	2.3	3.3	6.80	7.5	3	8.1	≥240
実施例 6	>200	2.3	3.3	6.50	7	3	8.0	≥240
比較例 4	—	2.3	3.0	8.80	7.5	3	7.8	≥240

[0057] In the porosity film of Examples 1-6 acquired by irradiating with ultraviolet rays from the result of Table 1, improvement in a void content and breathability is accepted, heat resistance and intensity being maintained compared with the porosity film of the comparative examples 1-4 corresponding to each example which manufactured without irradiating with ultraviolet rays. In the porosity film produced from comparison of Examples 3 and 4 and Examples 5 and 6 by irradiating 250 nm or less with the ultraviolet rays which do not have distribution of wavelength, it turns out that a strong fall does not arise.

[0058]

[Effect of the Invention] By this invention, a void content and breathability improve and a mechanical strength and contraction, [good] It is possible to produce the porosity film which consists of crosslinked polymers, and again, In [it is possible to produce the cell or capacitor which has the characteristic of a good request by using the porosity film obtained as a separator for cells, and] the bottom of an abnormal condition, Also when exposed to an elevated temperature in a cell, the shape and the mechanical strength of this separator are held, and since the state where the anode and the negative electrode were separated is maintainable, the safety of a cell or a capacitor can be raised.

[Translation done.]